Atomic structure: some concepts

- *The Schrödinger equation describes accurately the interactions of particles within potential fields*, such as electrons within atoms.

- Solving the Schrödinger equation directly for complicated atoms is extremely difficult. In fact, *only the hydrogen atom is generally solved directly*; atoms of atomic number greater than one are usually handled by techniques involving approximations.

- The hydrogen atom solution is also important in identifying the basic *selection rules for describing* ***allowed electron energy levels***. These quantum mechanical results must coincide with the experimental spectra, and we expect the energy levels to include those predicted by the Bohr model.

Atomic structure: the hydrogen atom

- Finding the wave functions for the hydrogen atom requires a solution of the Schrödinger equation in three dimensions for a coulombic potential field.

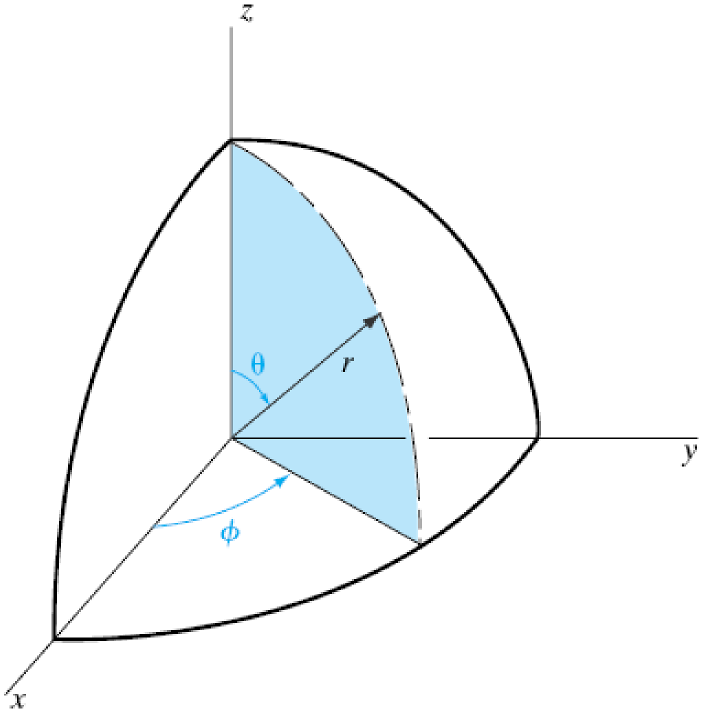
Since the problem is spherically symmetric, the *spherical coordinate system* is used in the calculation.

$$\boxed{-\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi = -\frac{\hbar}{j}\frac{\partial\Psi}{\partial t}} \qquad (2\text{–}24)$$

The term V(x, y, z) must be replaced by V(r,θ,Φ), representing the Coulomb potential which the electron experiences in the vicinity of the proton.

$$V(r,\theta,\phi) = V(r) = -(4\pi\epsilon_0)^{-1}\frac{q^2}{r}$$

The Coulomb potential varies only with r in spherical coordinates



When the separation of variables is made, the time-independent equation can be written as:

$$\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$$

- The wave functions are found in three parts. Separate solutions must be obtained for the *r*-dependent equation, the θ-dependent equation, and the ϕ-dependent equation. *After these three equations are solved, the total wave function is obtained from the product*.

- As in the simple potential well problem, each of the three hydrogen atom equations gives a solution which is quantized. Thus we would expect a *quantum number to be associated with each of the three parts of the wave equation*.

$$\psi_{nlm}(r, \theta, \phi) = R_n(r)\Theta_l(\theta)\Phi_m(\phi) \qquad (2\text{–}45)$$

These restrictions are summarized as follows:

$$\mathbf{n} = 1, 2, 3, \ldots \qquad (2\text{–}46\text{a})$$

$$\boldsymbol{l} = 0, 1, 2, \ldots, (\mathbf{n} - 1) \qquad (2\text{–}46\text{b})$$

$$\mathbf{m} = -\boldsymbol{l}, \ldots, -2, -1, 0, +1, +2, \ldots, +\boldsymbol{l} \qquad (2\text{–}46\text{c})$$

- In addition to the three quantum numbers arising from the three parts of the wave equation, there is an important quantization condition on the “spin” of the electron. *The intrinsic angular momentum* ***s*** *of an electron* with nlm specified is:

$$s = \pm \frac{\hbar}{2}$$

- In units of $\hbar$, the electron has a spin of ½, and *the angular momentum produced by this spin is positive or negative depending on whether the electron is “spin up” or “spin down”*.

- The important point for our discussion is that ***each allowed energy state of the electron in the hydrogen atom is uniquely described by four quantum numbers: n, l, m, s.***

n= 1, 2, 3, 4 … The *principal quantum number* has a dependence only on the distance between the electron and the nucleus (ie, the radial coordinate, r).

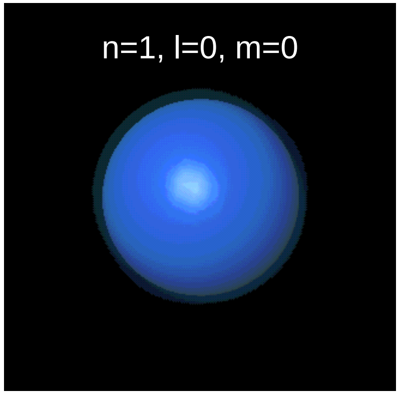
l= 0, 1, … n–1 The *azimuthal quantum number* gives the orbital angular momentum. In chemistry, this quantum number is very important, since it specifies the shape of an atomic orbital and strongly influences chemical bonds and bond angles.

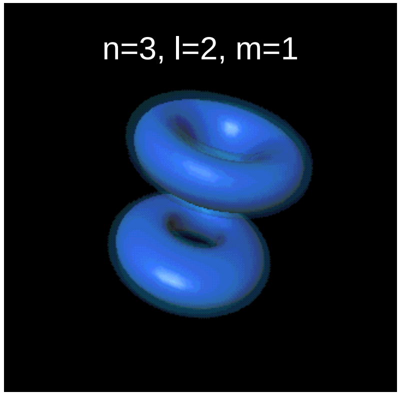
m= −l, −l+1 ... 0 ... l−1, l The *magnetic quantum number* is the projection of the orbital angular momentum along a specified axis.

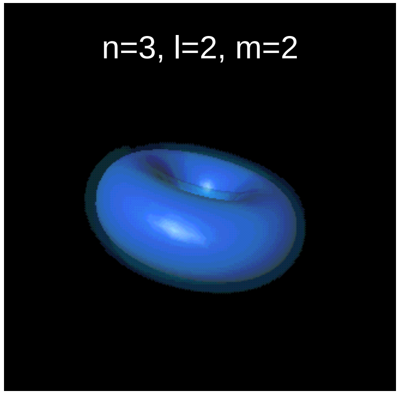
s= −1/2 or +1/2 The *spin quantum number* is the intrinsic angular momentum of the electron.

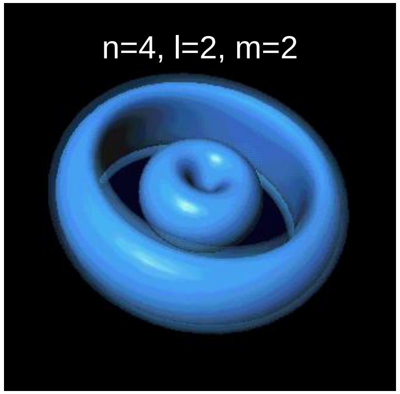
The periodic table

- The quantum number selection rules are valid for more complicated structures, and we can use these rules to gain an understanding of the ***arrangement of atoms in the periodic table of chemical elements***.









The Pauli exclusion principle states that *no two electrons in an interacting system can have the same set of quantum numbers n, l, m, s*. In other words, only two electrons can have the same three quantum numbers n, l, m, and those two must have opposite spin.

$\mathbf{n} = 1, 2, 3, \ldots$

$l = 0, 1, 2, \ldots, (\mathbf{n} - 1)$

$\mathbf{m} = -l, \ldots, -2, -1, 0, +1, +2, \ldots, +l$

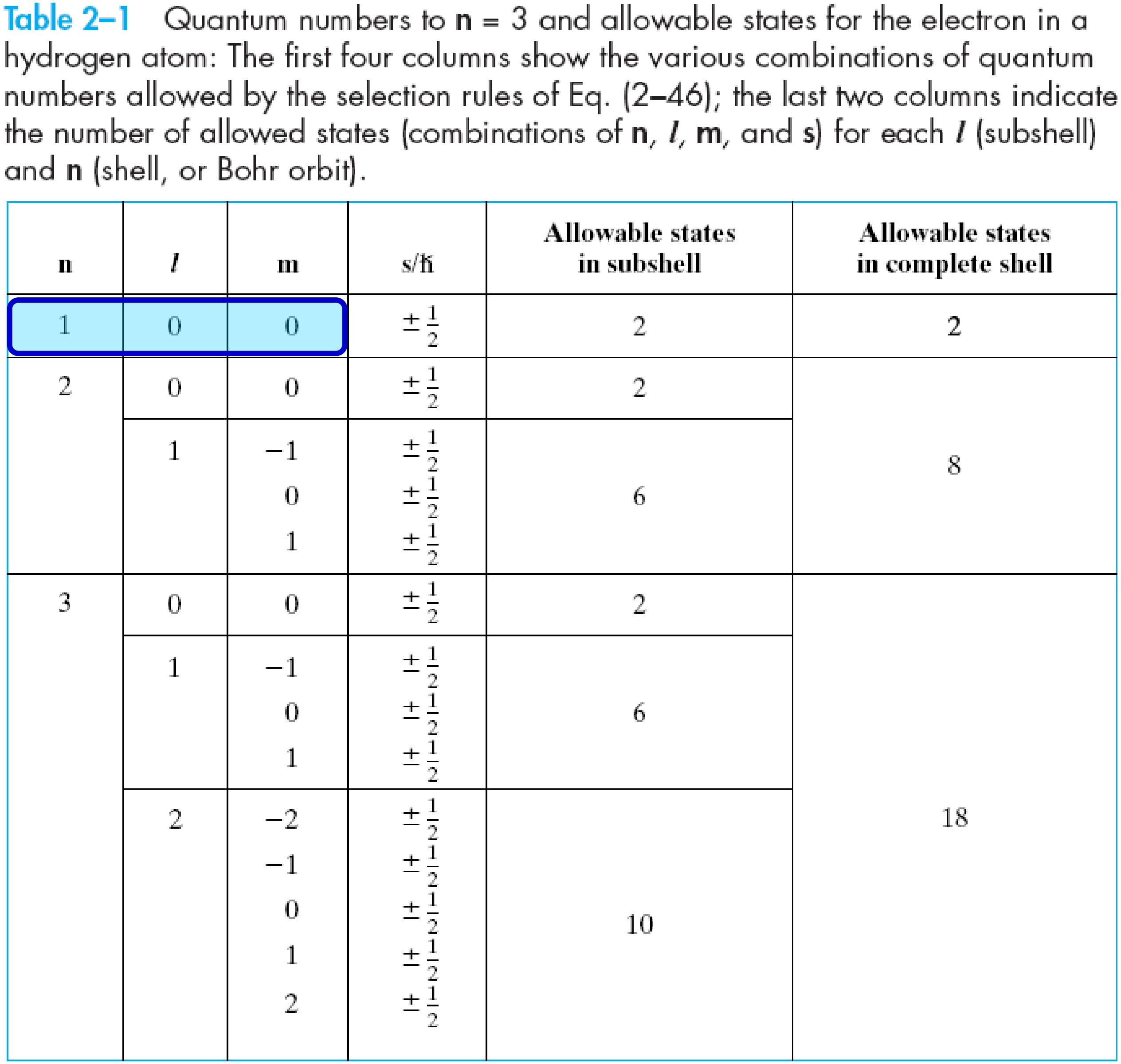


Table 2–1 Quantum numbers to **n** = 3 and allowable states for the electron in a hydrogen atom: The first four columns show the various combinations of quantum numbers allowed by the selection rules of Eq. (2–46); the last two columns indicate the number of allowed states (combinations of **n**, ***l***, **m**, and **s**) for each ***l*** (subshell) and **n** (shell, or Bohr orbit).

n	*l*	m	s/ħ	Allowable states in subshell	Allowable states in complete shell
1	0	0	$\pm\frac{1}{2}$	2	2
2	0	0	$\pm\frac{1}{2}$	2	8
	1	−1	$\pm\frac{1}{2}$	6	
		0	$\pm\frac{1}{2}$		
		1	$\pm\frac{1}{2}$		
3	0	0	$\pm\frac{1}{2}$	2	18
	1	−1	$\pm\frac{1}{2}$	6	
		0	$\pm\frac{1}{2}$		
		1	$\pm\frac{1}{2}$		
	2	−2	$\pm\frac{1}{2}$	10	
		−1	$\pm\frac{1}{2}$		
		0	$\pm\frac{1}{2}$		
		1	$\pm\frac{1}{2}$		
		2	$\pm\frac{1}{2}$		

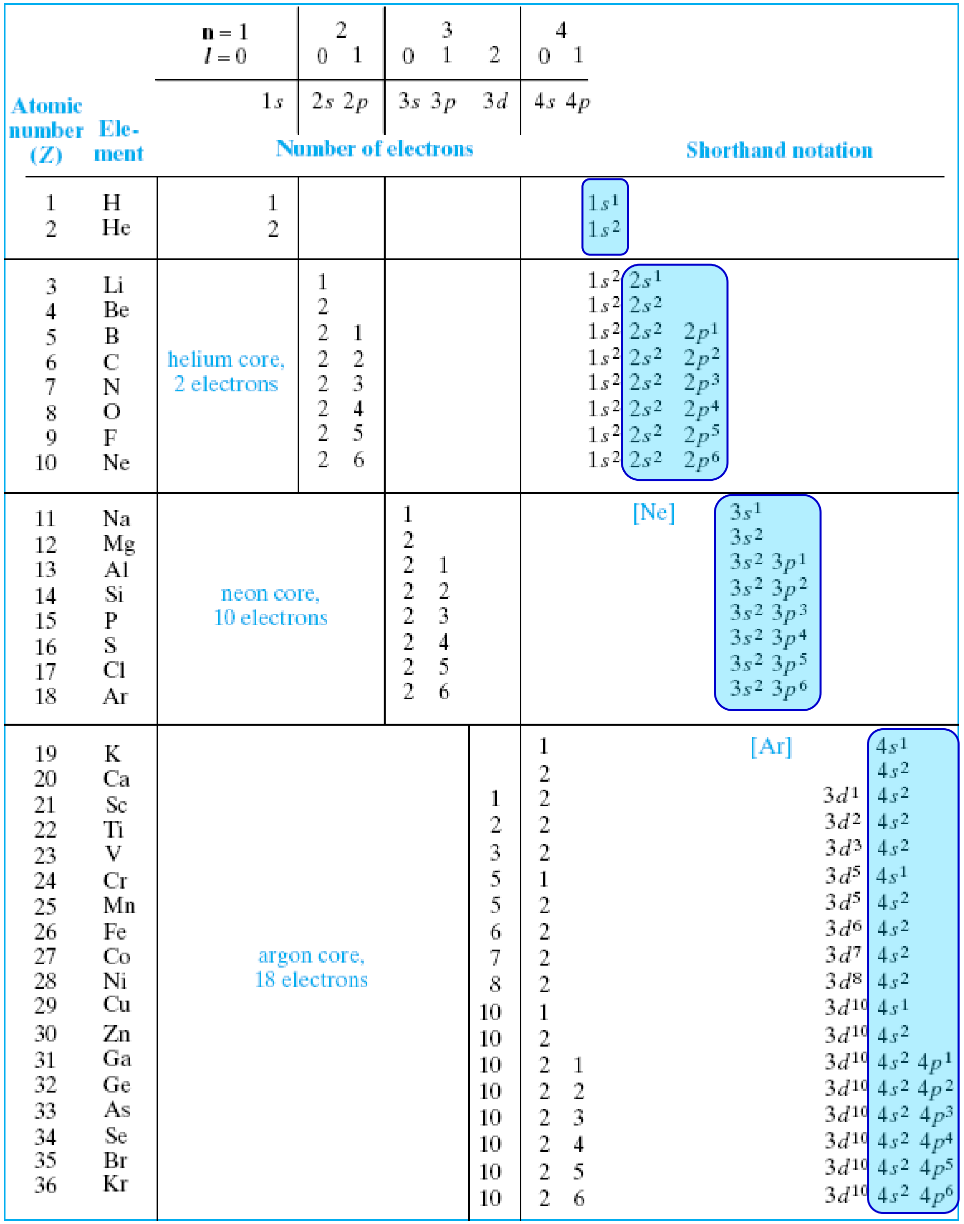
ψ_{100} state

$2n^2$

By listing the various combinations of quantum numbers, we can determine *into which shell each electron of a complicated atom fits, and how many electrons are allowed per shell*.

B, C, Si, P, Ge, As, HF, KCl, HCl …

Table 2–2 Electronic configurations for atoms in the ground state.

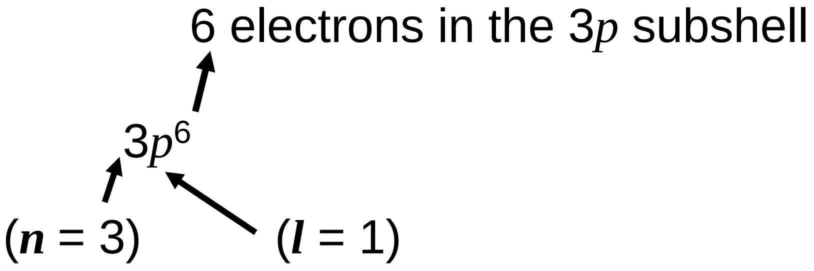


Atomic number (Z)	Element	n = 1, l = 0: 1s	2, l = 0: 2s	2, l = 1: 2p	3, l = 0: 3s	3, l = 1: 3p	3, l = 2: 3d	4, l = 0: 4s	4, l = 1: 4p	Shorthand notation
1	H	1								$1s^1$
2	He	2								$1s^2$
3	Li	helium core, 2 electrons	1							$1s^2\ 2s^1$
4	Be		2							$1s^2\ 2s^2$
5	B		2	1						$1s^2\ 2s^2\ 2p^1$
6	C		2	2						$1s^2\ 2s^2\ 2p^2$
7	N		2	3						$1s^2\ 2s^2\ 2p^3$
8	O		2	4						$1s^2\ 2s^2\ 2p^4$
9	F		2	5						$1s^2\ 2s^2\ 2p^5$
10	Ne		2	6						$1s^2\ 2s^2\ 2p^6$
11	Na	neon core, 10 electrons			1					[Ne] $3s^1$
12	Mg				2					$3s^2$
13	Al				2	1				$3s^2\ 3p^1$
14	Si				2	2				$3s^2\ 3p^2$
15	P				2	3				$3s^2\ 3p^3$
16	S				2	4				$3s^2\ 3p^4$
17	Cl				2	5				$3s^2\ 3p^5$
18	Ar				2	6				$3s^2\ 3p^6$
19	K	argon core, 18 electrons						1		[Ar] $4s^1$
20	Ca							2		$4s^2$
21	Sc						1	2		$3d^1\ 4s^2$
22	Ti						2	2		$3d^2\ 4s^2$
23	V						3	2		$3d^3\ 4s^2$
24	Cr						5	1		$3d^5\ 4s^1$
25	Mn						5	2		$3d^5\ 4s^2$
26	Fe						6	2		$3d^6\ 4s^2$
27	Co						7	2		$3d^7\ 4s^2$
28	Ni						8	2		$3d^8\ 4s^2$
29	Cu						10	1		$3d^{10}\ 4s^1$
30	Zn						10	2		$3d^{10}\ 4s^2$
31	Ga						10	2	1	$3d^{10}\ 4s^2\ 4p^1$
32	Ge						10	2	2	$3d^{10}\ 4s^2\ 4p^2$
33	As						10	2	3	$3d^{10}\ 4s^2\ 4p^3$
34	Se						10	2	4	$3d^{10}\ 4s^2\ 4p^4$
35	Br						10	2	5	$3d^{10}\ 4s^2\ 4p^5$
36	Kr						10	2	6	$3d^{10}\ 4s^2\ 4p^6$

The only new convention to remember in this notation is the naming of the ***l*** values:

$$l = 0, 1, 2, 3, 4, \ldots$$
$$s, p, d, f, g, \ldots$$

This convention was created by early spectroscopists who referred to the first four spectral groups as *s*harp, *p*rincipal, *d*iffuse, and *f*undamental. Alphabetical order is used beyond *f*. With this convention for ***l***, we can write an electron state as follows:



6 electrons in the 3*p* subshell

$3p^6$

(***n*** = 3)

(***l*** = 1)

For example, the total electronic configuration for Si (Z=14) in the ground state is $1s^22s^22p^63s^23p^2$

$1s^2 2s^2 2p^6 3s^2 3p^2$

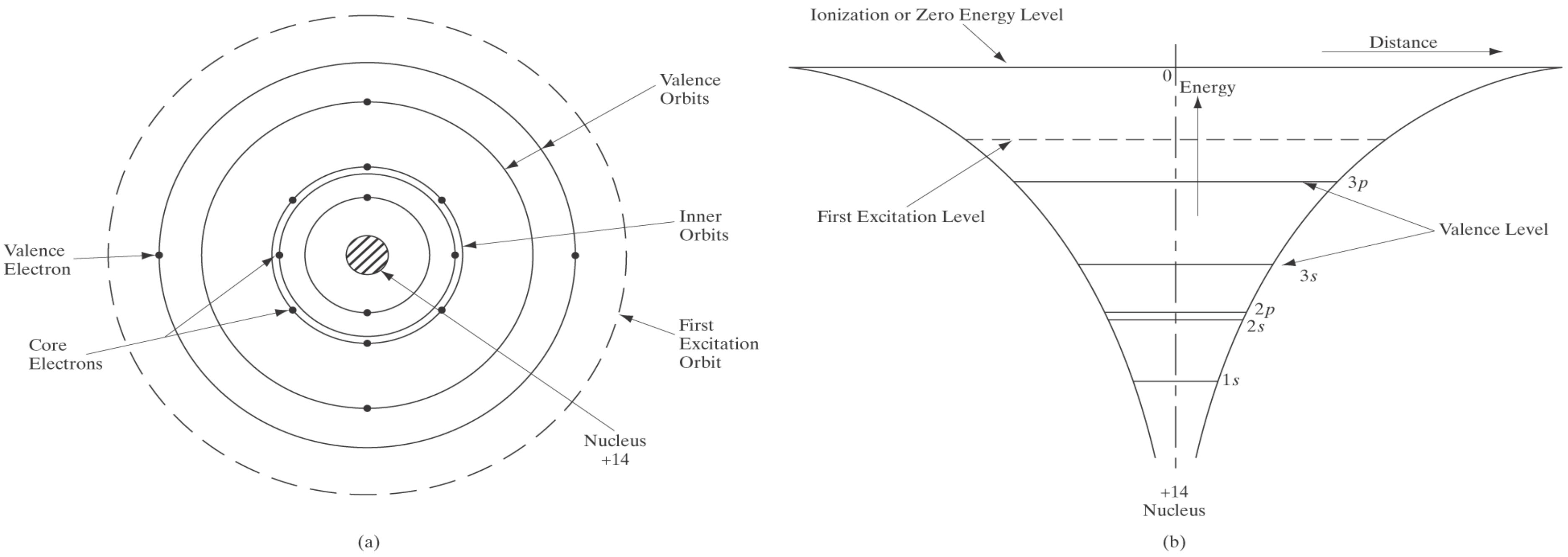


Figure 2.8

Electronic structure and energy levels in a Si atom: (a) The orbital model of a Si atom showing the 10 core electrons (**n** = 1 and 2), and the 4 valence electrons (**n** = 3); (b) energy levels in the coulombic potential of the nucleus are also shown schematically.